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(54) Toner for electrostatic images.

(57) A toner for developing electrostatic images containing a resin selected from a saturated polyester resin, an acrylic resin, and an epoxy resin as a binder resin component, wherein said resin has a carboxyl group or a glycidyl group and is used as a resin composition contining (a) from 0.5 to 10 parts by weight of a polyfunctional cyanic acid ester having at least two cyanato groups in the molecule or a prepolymer of the cyanic acid ester per 100 parts by weight of the resin and (b) a curing catalyst for the component (a).

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TONER FOR ELECTROSTATIC IMAGES

FIELD OF THE INVENTION

This invention relates to a toner for developing electrostatic images formed in an electrophotographic method, an electrostatic photographic method, an electrostatic recording method, etc.

BACKGROUND OF THE INVENTION

In general, electrostatic images are developed by a toner which is a coloring powder to form toner images and the toner images are fixed as they are or after being transferred onto a transfer paper, etc.

The toner is usually prepared by melt-mixing components mainly composed of a polymer as a binder component, carbon black and/or other coloring agent, and a charge controlling agent.

It is well known that the performance of the toner is greatly influenced by the binder component and polyester series resins, acrylic resins, etc., are used as the binder component. However, a binder resin which satisfies both the performances of a low-temperature fixing property which is the most important property for toner, and a prevention of the occurrence of an offset phenomenon, and is also excellent in producibility has not yet been found or developed.

A low-temperature fixing property is a property inevitable for efficiently forming toner images and, on the other hand, the occurrence of an offset phenomenon, that is, the phenomenon that a part of toner components is transferred onto a heat roller which is usually used for fixing toner images, and stains the surfaces of transfer papers being supplied thereafter or is further transferred onto a press roller which is pressed onto the heat roller, and stains the back surfaces of transfer papers,must be prevented.

The fixing property of toner is a property originally incompatible with the prevention of the offset phenomenon of the toner but it is a theme to be solved without fail at the practice of toners to prevent the occurrence of the offset phenomenon while keeping the low-temperature fixing property of the toners.

As the means for solving the above problem, there are a method of using a binder resin having a large molecualr weight formed by using a tri- or more-functional monomer as the raw material for the polymer resin and partial-crosslinking the monomer as disclosed in, for example, US Patent 3,938,992 and RE 31,072; a method of incorporating a crosslinking agent in a binder resin composition and partial-crosslinking the resin composition; and a method of using a binder composition composed of a large molecular weight component and an ordinary molecular weight component.

In those binder resins, polyester series resins are known as a binder resin having high performance but have a disadvantage that when a tri- or more-functional monomer such as trimellitic acid, etc., is used as the monomer component, there are no any effective manners to stop the polymerization reaction for obtaining the polymer having a desired molecular weight and a desired degree of crosslinking other than lowering tenperature which makes it difficult to widely and positively promote the use of the toner using the polyester series resin in spite of excellent properties of the resin.

Also, in the method of incorporating a crosslinking agent to a binder composition and partial-crosslinking the binder composition, the binder resin obtained is inferior in performance to the binder resin obtained by the method of using a tri- or more-functional monomer as the monomer component and thus has not yet been used for practice purpose.

SUMMARY OF THE INVENTION

As the results of various investigations to overcome the above-described problems, it has been found that a desired toner for electrostatic images is obtained by using a polyfunctional cyanic acid ester having at least 2 cyano groups in the molecule or a prepolymer of the cyanic acid ester and a curing catalyst for the cyanic acid ester or the prepolymer as a partial crosslinking agent for the resin composition. The present has been accomplished based on this novel finding.

Accordingly, an object of the present invention is a to provide a toner for developing electrostatic images, containing a resin selected from a saturated polyester resin, an acrylic resin, and an epoxy resin as

a binder component, wherein the resin has a carboxy group or a glycidyl group and is used as a resin composition containing (a) from 0.5 to 10 parts by weight of a functional cyanic acid ester having 2 or more cyano groups in the molecule or a prepolymer of the cyanic acid ester per 100 parts by weight of the resin and (b) a curing catalyst for the component (a).

In the preferred embodiments of this invention,

the curing catalyst (b) for the component (a) is previously compounded in the resin composition in a step of from the completion of the polymerization of the resin to the recovery (separation) of the polymerization product;

the curing catalyst (b) for the component (a) is an organic metal compound;

the resin composition is prepared by mixing the components at a temperature of from 100°C to 200°C;

the resin composition is prepared by mixing a coloring agent with the other necessary components for toner;

the resin is a saturated polyester resin having a glass transition temperature of from 30°C to 75°C and an acid value of at least 10 KOHmg/g;

the resin is an acrylic resin having a glass transition temperature of from 30°C to 75°C and an acid value of from 2 to 50 KOHmg/g;

the resin is an acrylic resin having a glass transition temperature of from 30°C to 75°C and a glycidyl group equivalent of from 1000 to 20,000; and

the resin is a bisphenol A type epoxy resin having a melting point of from 60°C to 160°C.

DETAILED DESCRIPTION OF THE INVENTION

Then, the construction of this invention is explained in detail.

The resin as a raw material for the binder of the toner of this invention is selected from a saturated polyester resin, an acrylic resin, and an epoxy resin which are conventionally known as a binder resin,and has a carboxyl group and/or a glycidyl group.

Saturated Polyester Resin

The saturated polyester resin for use in this invention has preferably a glass transition temperature of from 30°C to 75°C and an acid value of at least 10 KOHmg/g, has a carboxyl group, and is obtained by condensing an optional acid component and a polyhydric alcohol component.

Examples of the acid component are terephthalic acid, isophthalic acid, o-phthalic acid, malonic acid, dimethylmalonic acid, succinic acid, glutaric acid, adipic acid, trimethyladipic acid, pimelic acid, 2,2-dimethylglutaric acid, azelaic acid, sebacic acid, 1,3-cyclopentanedicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 2,5-norbornanedicarboxylic acid, 1,4-naphthalic acid, diphenic acid, 4,4′-oxybenzoic acid, diglycolic acid, thiodipropionic acid, 2,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, benzoic acid, rosin, and resin derivatives such as hydrogenated rosin and disproportionated rosin.

Those acids may be acid anhydrides, esters, chlorides, etc., and include, for example, dimethyl 1,4-cyclohexanedicarboxylate, dimethyl 2,6-naphthalenedicarboxylate, dimethyl isophthalate, dimethyl terephthalate, and diphenyl terephthalate. Furthermore, unsaturated carboxylic acids such as maleic acid (anhydride), fumaric acid, etc., or trihydric or higher hydric carboxylic acids such as trimellitic acid, trimellitic anhydride, pyrromellitic acid, pyrromellitic anhydride, 4-methylcyclohexene-1,2,3-tricarboxylic acid anhydride, trimesic acid, etc., can be used if the amount thereof is small.

Examples of the polyhydric alcohol are ethylene glycol, diethylene glycol, propylene glycol, 1,3-propanediol, 2,4-dimethyl-2-ethylhexane-1,3-diol, 2,2-dimethyl-1,3-propanediol (neopentyl glycol), 2-ethyl-2-isobutyl-1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 2,2,4-trimethyl-1,6-hexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, 4,4′-thiodiphenol, 4,4′-(2-norbornidene)-diphenol, 4,4′-dihydroxybiphenol, o-dihydroxybenzene, m-dihydroxybenzene, p-dihydroxybenzene, 4,4′-isopropylidenephenol, 4,4′-isopropylidenebis(2,6-dichlorophenol), 2,5-naphthalenediol, and p-xylenediol.

Furthermore, trihydric or higher hydric alcohols such as pentaerythritol, dipentaerythritol, tripentaerythritol, glycerol, trimethylolpropane, trimethylolethane, 1,3,6-hexanetriol, etc., can be used if the amount is small. Also, a compound having a hydroxyl group and a carboxyl group in the molecule, such as a low

molecular weight condensate of terephthalic acid and ethylene glycol, can be used.

In addition to the above acid component and the polyhydric alcohol component, a sulfonate group can be introduced into the resin by a conventional method. Typical examples of the condensing component for use in such a case are 5-sodiosulfoisophthalic acid and 5-potassium-sulfoisophthalic acid,although the invention is not limited to those compounds.

For producing the polyester resin by condensing the above acid component and polyhydric alcohol, an optional conventionally known method can be used without need of a specific operation.

In a typical example, the acid component and the polyhydric alcohol of from 1.0 to 1.5 times the amount of the acid component are placed in a reaction vessel together with a catalyst and a dehydrocondensation reaction is carried out with the increase of temperature to 140°C to 260°C. As the catalyst for use in this case, there are zinc acetate, zinc chloride, lauryltin oxide, butyltin oxide, octyltin oxide, etc., and the catalyst is usually used in an amount of from 0.05 to 0.15 wt% based on the weight of the dicarboxylic acid. A solvent is not always necessary for the reaction but, if desired, an inert solvent such as methyl acetate, benzene, acetone, xylene, toluene, etc., may be used.

The polyester resin for use in this invention is as described above but it is particularly preferred that the glass transition temperature thereof is from 45°C to 70°C and the acid value is from 20 to 60 KOHmg/g. Also, it is preferred that the the number average molecular weight thereof is from 3,000 to 8,000 and the weight average molecular weight thereof is at least 1.0×10^4, and in particular from 5.0×10^4 to 50×10^4.

Acrylic Resin

The acrylic resin for use in this invention has preferably an acid value of from 2 to 50 KOHmg/g or a glycidyl group equivalent of from 1,000 to 20,000, has a carboxyl group and/or a glycidyl group, and has a glass transition temperature of from 30 to 75°C. The acrylic resin is obtained by polymerizing an alkyl ester component of acrylic acid or methacrylic acid (hereinafter, is referred to as (meth)acrylic acid) and a glycidyl ester component of an unsaturated carboxylic acid or (meth)acrylic acid.

Examples of the (meth)acrylic acid alkyl ester are the esters such as methyl ester, ethyl ester, propyl ester, butyl ester, 2-ethylhexyl ester, lauryl ester, stearyl ester, etc., of (meth)acrylic acid. Also, examples of the unsaturated carboxylic acid component are (meth)acrylic acid, maleic acid, crotonic acid, etc.

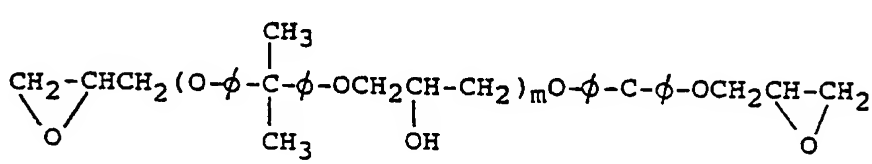
In this invention, if necessary, a copolymerizable monomer such as a vinyl ester (e.g., (meth)acrylic acid hydroxyalkyl ester, (meth)acrylic acid alkylene glycol, (meth)acrylamide, (meth)acrylonitrile, dialkylamino (meth)acrylate, styrene, and vinyl acetate may be further copolymerized with above-described components.

For producing the acrylic resin, there are no particular restrictions and an optional known means can be used. The production thereof is usually carried out by a solution polymerization using a solvent such as methyl acetate, acetone, benzene, xylene, toluene, etc., in the presence of a radical catalyst, and by removing the remaining monomers and the solvent from the reaction mixture obtained, the acrylic resin for the toner binder is obtained.

It is preferred that the acrylic resin has the acid value of from 5 to 30 KOHmg/g or the glycidyl group equivalent of from 1,200 to 8,000, the glass transition temperature of from 45°C to 70°C, and the weight average molecular weight of from 2.0×10^4 to 10×10^4.

Epoxy Resin

The epoxy resin for use in this invention is preferably a di-functional bisphenol A type epoxy resin having a melting point of from 60°C to 160°C, and is preferably shown by following formula (1), and the epoxy equivalent of the resin is preferably from 600 to 6,000, and particularly preferably from 800 to 3,500.



(1)

wherein ϕ represents a benzene nucleus of 1,4-bond and m is usually from about 2 to about 4.

Cyanato Compound

The polyfunctional cyanic acid ester having at least two cyanato groups (-OCN) in the molecule or a prepolymer of the cyanic acid, which is the component (a) being compounded with the polyester resin, acrylic resin or epoxy resin in this invention, is preferably a compound represented by following formula (2)

$R(OCN)_n$ (2)

wherein R represents an aromatic organic group which may include a heterocyclic ring, the cyanato group being bonded to the aromatic ring of the organic group, and n is an integer of 2 or more, and is usually not more than 5.

Specific examples of the cyanato compound are 1,3-dicyanatobenzene, 1,4-dicyanatobenzene, 1,3,5-tricyanatobenzene, 1,3-, 1,4-, 1,6-, 1,8-, 2,6- or 2,7-dicyanatonaphthalene, 1,3,6-tricyanatonaphthalene, 4,4′-dicyanatobiphenyl, bis(4-dicyanatophenyl)methane, bis(3,5-dimethyl-4-dicyanatophenyl)methane, 2,2-bis(4-cyanatophenyl)propane, 2,2-bis(3,5-dichloro-4-cyanatophenyl)propane, 2,2-bis(3,5-dibromo-4-cyanatophenyl)propane, 2,2-bis(3,5-dimethyl-4-cyanatophenyl)propane, bis(4-cyanatatophenyl) ether, bis(4-cyanatophenyl) thioether, bis(4-cyanatophenyl)sulfone, tris(4-cyanatophenyl) phosphite, tris(4-cyantophenyl) phosphate, polyfunctional novolak cyanates obtained by the reaction of novolak and cyanogen halides (U.S. Patents 4,022,755 and 3,448,079), polyfunctional polycarbonate cyanates obtained by the reaction of polycarbonate oligomers having a hydroxyl group at the terminal and cyanogen halides (U.S. Patent 4,026,913 and German Patent 2,611,796), and styryl-pyridine-cyanates obtained by the reaction of polyhydroxystyryl-pyridine, etc., which are obtained by reacting hydroxybenzaldehydes and alkyl-substituted pyridines, and cyanogen halides (U.S. Patent 4,578,439).

Other examples of the cyanato compounds which can be also used in this invention are described in U.S. Patents 3,553,244, 3,755,402, 3,740,348, 3,595,900, 3,694,410, and 4,116,946, British Patents 1,305,967 and 1,060,933, and German Patents 1,190,184 and 1,195,764).

Also, the above polyfunctional cyanic acid esters can be used as prepolymers obtained by polymerizing the cyanic acid esters in the presence of a mineral acid, Lewis acid, a salt (such as sodium carbonate, lithium chloride, etc.), or a phosphoric acid ester (such as tributylphosphine, etc.) or as prepolymers of the cyanic acid esters and polyfunctional amines.

As the catalyst for the component (a) in this invention, any catalysts capable of accelerating curing of the component (a) can be usually used.

Examples of such a catalyst are organic peroxides such as benzoyl peroxide, lauroyl peroxide, capryl peroxide, acetyl peroxide, p-chlorobenzoyl peroxide, di-tert-butyl di-peroxide, etc.; azo compounds such as azobisnitrile, etc.; imidazoles such as 2-methylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2-phenylimidazole, 2-ethyl-4-methylimidazole, 1-benzyl-2-methylimidazole, 1-propyl-2-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-ethylimidazole, 1-cyanoethyl-2-undecylimidazole, 1-cyanoethyl-2-phenylimidazole, 1-cyanoethyl-2-ethyl-4-methylimidazole, 1-guanaminoethyl-2-methylimidazole, etc.; the addition products of those imidazoles and a carboxylic acid or the anhydride thereof; tertiary amines such as N,N-dimethylbenzylamine, N,N-dimethylaniline, N,N-dimethyltoluidine, N,N-dimethyl-p-anisidine, p-halogeno-N,N-dimethylaniline, 2-N-ethylanilinoethanol, tri-n-butylamine, pyridine, quinoline, N-methylmorpholine, triethanolamine, triethylenediamine, N,N,N′,N′-tetramethylbutanediamine, N-methylpiperidine, etc.; phenols such as phenol, xylenol, cresol, resorcinol, catechol, fluoroglycine, etc.; organic metal salts such as lead naphthenate, lead stearate, zinc naphthenate, zinc octylate, tin oleate, stannous laurate, dibutyltin maleate, manganese naphthenate, cobalt naphthenate, acetylacetone iron, etc.; the solutions of the above organic metal salts dissolved in hydroxyl group-containing compounds such as phenol, bisphenol, etc.; organotin compounds such as dibutyltin oxide, dioctyltin oxide, alkyltins, other alkyltin oxides, etc.; inorganic metal salts such as $SnCl_3$, $ZnCl_2$, $AlCl_3$, etc.; and acid anhydrides such as maleic anhydride, phthalic anhydride, lauric anhydride, pyromellitic anhydride, trimellitic anhydride, hexahydrophthalic anhydride, hexahydromellitic anhydride, hexahydropyromellitic anhydride, etc. In those catalysts, organic metal compounds such as organic metal salts and organotin compounds (e.g., dibutyltin oxide, dioctyltin oxide, alkyltins, alkyltin oxides, etc.) are preferred.

Also, the amount of the catalyst in this invention is in the range of a general catalyst and is, e.g., from few percents by weight to 10% by weight based on the weight of component (a).

Preparation of Toner

The compounding amount of the component (a) in this invention is from 0.5 to 10 parts by weight, preferably from 1.0 to 5 parts by weight, and particularly preferably from 1.0 to 2.5 parts by weight,per 100 parts by weight of the raw material resin for binder. If the compounding amount thereof is less than 0.5 part by weight, the effect of this invention is reluctant to obtain, while if the amount is over 10 parts by weight, an excessive crosslinking reaction undesirably occurs to increase the fluidity initiation temperature.

The toner of this invention is prepared by melt-mixing a mixture of the resin composition, a coloring agent, and, if necessary, a charge controlling agent; by adding the component (a), the component (b), a coloring agent, and, if necessary, a charge controlling agent to the raw material resin for the binder in place of using the resin composition in this invention followed by melt-mixing; or by producing a so-called master batch composed of the raw material resin for binder compounded with large amounts of the component (a) and the component (b) and melt-mixing the master batch with the raw material resin for binder, a coloring agent, and, if necessary, a charge controlling agent. Also, it is preferred that compounding or mixing of the above components is carried out by using an extruder, a press-type kneader, double rolls, etc., at a melt-mixing temperature of from 100°C to 200°C, and more preferably from 120°C to 180°C, for a melt-mixing time of from about 5 minutes to 30 seconds.

Examples of the coloring agent for use in this invention are carbon black, Nigrosine dyes, Aniline Blue, Chalco Oil Blue, chrome yellow, ultramarine blue, Do Pont Oil Red, Quinoline Yellow, Methylene Blue Chloride, Phthalocyanine Blue, Malachite Green Oxalate, Lamp Black, Rose Bengale, etc.

At the preparation of the toner of this invention, if necessary, other resins for binder having no functional group than the above saturated polyester resin, acrylic resin, or epoxy resin having a carboxy group or a glycidyl group, which is the main component for the toner of this invention, and waxes such as polyolefin wax, etc., can be added to the resin composition as assistants.

In addition, when a metal-coordinated compound such as Phthalocyanine Blue, etc., is used at the preparation of the toner, it sometimes happens that the component (a) reacts with the coloring agent to cause a decoloring reaction and hence in such a case, it is preferred to use the component (a) as a composition or a master batch thereof previously compounded with the raw material resin for the binder.

Then, the invention is explained by the following examples, in which all parts and percents (%), unless otherwise indicated, are by weight. Also, the physical properties were measured as follows.

Glass Transition Temperature:

Measured by DSC-Type 7, trade name, manufactured by Perkin Elmer Co.

Melt Viscosity:

Measured by Flow Tester CFT-500, trade name, manufactured by Shimazu Corporation.
Measurement Condition: Orifice diameter 1 mm, length 10 mm, load 30 kg.

Mean Particle Size:

Measured by Coal Tar Multisizer, manufactured by Coal Tar Electronics Co.

Electrostatic Charge Amount:

After stirring 95 parts of an iron powder (TEFV 200/300, manufactured by Nippon Teppun K.K.) and 5 parts of a toner for 10 minutes by a rotary mixer, the charged amount was measured by a blow off type charge measurement machine, manufactured by Toshiba Corporation.

<u>Ordinary Density and Density Retension of Images</u>

The ordinary density of images was measured using Mending Tape No. 810 (made by Sumitomo 3M Co.) and the density retention thereof was measured by a Macbeth densitometer (manufactured by Macbeth Co.).

Example 1

Production of Polyester Resin

In a one liter four neck flask equipped with a packed column were placed 0.8 mol of terephthalic acid, 0.2 mol of isophthalic acid, 0.4 mol of ethylene glycol, 0.6 mol of a bisphenol A-propylene oxide addition product, 0.03 mol of glycerol, and 0.0003 mol of dibutyltin oxide and the mixture was stirred for 2 hours at 180°C in a nitrogen gas atmosphere. Then, the temperature of the system was raised to 240°C and the reaction was further continued. When flowing out of water was stopped, the temperature of the system was lowered to 180°C and after further adding thereto 0.1 mol of phthalic anhydride, the reaction was further performed for 30 minutes at 180°C.

The supply of nitrogen gas was stopped and after adding thereto 0.0015 mol of dibutyltin oxide as a curing catalyst for preparing toner, the mixture was stirred for 30 minutes at a reduced pressure of 500 mmHg to finish the reaction.

The acid value of the polyester resin obtained was 30 KOHmg/g, the melt viscosity thereof at 100°C was 2×10^4 poise, and the glass transition temperature was 62°C.

Production of Toner

A mixture of 88 parts of the above polyester resin, 9 parts of carbon black #44 (trade name, made by Mitsubishi Kasei Corporation), 1 part of Bontoron S-34 (trade name, made by Orient Kagaku Kogyo K.K.), 2 parts of Biscoal 550p (trade name, made by Sanyo Chemical Industries, Ltd.), and 2 parts of 2,2-bis(4-cyanatophenyl) propane as powders was kneaded using a twin-screw extruder PCM-30 (trade name, manufactured by Ikegai Tekko K.K.) at 60°C for the 1st cylinder, 140°C for the 2nd and 3rd cylinders, a shaft rotation number of 100 r.p.m., and a supplying rate of 200 g/min.

The extruded product was roughly ground to an extent of passing a 1 mm sieve, then finely ground by a jet mill (manufactured by Nippon Pneumatic K.K.), and classified by a pneumatic classifier to provide a toner.

Property of the Toner

The melt viscosity of the toner at 140°C was 4×10^4 poise, the charging amount was -20μc/g, and the number average particle size was 0.5μm.

Image Test

A toner image was transferred onto a plain paper by an electrophotographic copying machine (manufactured by Mita Industrial Co., Ltd.) using a mixture of 5 parts of the toner obtained above and 95 parts of an iron powder TEFV 150/250 (manufactured by Nippon Teppun K.K.) and the paper having the toner image in an unfixed state was passed through a heat roll coated with Teflon (trade name, made by E.I. du Pont de Nemours & Co.) and a backup roll lined with rubber at a speed of 400 mm/sec. to fix the toner image.

When the temperature of the heat roll was changed from 160°C to 200°C, no attaching of the toner to the heat roll was observed and also the ordinary density and the density retention of the toner image each was 85% or higher, which showed sufficient fixing.

Comparison Example 1

The same procedure as in Example 1 except that 2,2-bis(4-cyanatophenyl)propane was not used was followed.

The melt visocisty of the toner obtained at 100°C was 3×10^4 poise, the charging amount was -22μc/g,

and the number average particle size was 9.3μm.

The result of the image test showed that the toner attached to the heat roll in all the cases of the heat roll temperature of 160°C, 170°C, 180°C, 190°C, and 200°C to cause offset and clear images were not obtained in each case.

Example 2

Production of Polyester Resin

In the same type of flask as used in Example 1 were placed 0.7 mol of terephthalic acid, 0.3 mol of isophthalic acid, 0.2 mol of ethylene glycol, 0.2 mol of disproportionated rosin monoglyceride, 0.6 mol of a bisphenol A-ethylene oxide addition product, 0.02 mol of trimethylolpropane, and 0.0003 mol of dibutyltin oxide,and the mixture was stirred at 240°C in a nitrogen gas atmosphere to perform the reaction. When the flow out of water stopped, the temperature of the system was lowered to 180°C and after further adding thereto 0.07 mol of trimellitic anhydride, the reaction was continued for 30 minutes.

The supply of nitrogen was stopped and after adding thereto 0.0015 mol of dibutyltin laurate as a curing catalyst for preparing toner, the mixture was further stirred for 30 minutes at a reduced pressure of 500 mmHg to finish the reaction.

The acid value of the polyester resin obtained was 32 KOHmg/g, the melt viscosity thereof at 100°C was 3 x 10^4 poise, and the glass transition temperature was 60°C.

Production of Toner

By following the same procedure as in Example 1 except that 4 parts of 1,4-dicyanatobenzene was used in place of 2 parts of 2,2-bis(4-cyanatophenyl)propane, a toner was obtained.

Property of the Toner

The melt viscosity of the toner at 140°C was 2 x 10^4 poise, the charging amount was -25μc/g, and the number average particle size was 9.8μm.

Image Test

When the same test as in Example 1 was followed, no attaching of the toner to the heat roll was observed and the density retention thereof measured using a mending tape was at least 85%.

Comparison Example 2

By following the same procedure as in Example 2 except that 1,4-dicyanatobenzene was not used, a toner was obtained.

The melt viscosity of the toner at 100°C was 5 x 10^4 poise, the charging amount was -28μc/g, and the number average particle size was 0.3μm.

The result of the image test showed that the toner attached to the heat roll in all the cases of the heat roll temperatures of 160°C, 170°C, 180°C, 190°C, and 200°C to cause offset and clear images were not obtained.

Example 3

Production of Acrylic Resin

In a four-neck flask equipped with a stirrer, a thermometer, and a condenser was placed 450 g of xylene and after raising the temperature thereof, 320 g of methyl methacrylate, 130 g of n-butyl methacrylate, 50 g of glycidyl methacrylate, and 5 g of a xylene solution of 20% benzyl peroxide were added dropwise into the flask. Then, the reaction was performed for about 13 hours while further adding 5 g of a xylene solution of 20% benzyl peroxide as described above every 2 hours.

Then, benzoyl peroxide was added to the reaction mixture as a curing catalyst for preparing toner in an amount of 0.1% to the resin. By removing the solvent and the residual monomers from the reaction mixture according to ordinary manner, a glycidyl group-containing acrylic resin having a glass transition temperaturee of 72°C, a glycidyl equivalent of 1,800, and a melt viscosity at 120°C of 1.6 x 10^4 poise was obtained.

Production and Property of Toner

By following the same procedure as in Example 1 except that the above acrylic resin was used in place of the saturated polyester, a toner was obtained.

The melt viscosity of the toner at 140°C was 6.5 x 10^4 poise, the charging amount was 15μc/g, and the number average particle size was 10.5μm.

Image Test

A toner image was transferred onto a plain paper by an electrophotographic copying machine DC-162 (manufactured by Mita Industrial Co., Ltd.) using a mixture of 5 parts of the toner obtained and 95 parts of an iron powder TEFV 150/250 (manufactured by Nippon Teppun K.K.) and the paper having the toner image in an unfixed state was passed through a heat roll coated with Teflon (trade name, made by Du Pont) and a backup roll lined with rubber at a speed of 400 mm/sec. to fix the image.

When the temperature of the heat roll was changed from 180°C to 220°C in this case, no attaching of the toner to the heat roll was observed. Also, the ordinary density and the density retention of the image each was at least 85%, which showed fixing being sufficient.

Comparison Example 3

By following the same procedure as in Example 3 except that 2,2-bis(4-cyanatophenyl)propane was not used, a toner was obtained.

The melt viscosity of the toner at 120°C was 2 x 10^4 poise, the charging amount was -16μc/g, and the number average particle size was 9.3μm.

The result of the image test showed that the toner attached to the heat roll in all the cases of the heat roll temperatures of 180°C, 190°C, 200°C, 210°C, and 220°C to cause offset and clear images were not obtained in each case.

Example 4

Production of Acrylic Resin

By following the same procedure as in Example 3 except that the amounts of the methacrylates were changed to 330 g of methyl methacrylate, 160 g of n-butyl methacrylate, and 10 g of glycidyl methacrylate, a glycidyl group-containing acrylic resin having a glass transition temperature of 71°C, a glycidyl group equivalent of 7,000, and a melt viscosity at 120°C of 1.2 x 10^4 poise was obtained.

Production and Property of Toner

By following the same procedure as in Example 1 except that the above acrylic resin was used in place of the saturated polyester and 4 parts of 1,4-dicyanatobenzene and 0.1 part of 2-phenylimidazole were used in place of 2 parts of 2,2-bis(4-cyanatophenyl)propane, a toner was obtained.

The melt viscosity of the toner obtained at 140°C was 4 x 10^4 poise, the charging amount was -18μc/g, and the number average particle size was 11.0μm.

Image Test

When the image test as in Example 3 was performed, no attaching of the toner to the heat roll was observed and the density retention of the images measured using a mending tape was at least 85%.

Comparison Example 4

By following the same procedure as in Example 4 except that the use of 4 parts of 1,4-dicyanatobenzene and 0.1 part of 2-phenylimidazole was omitted, a toner was obtained.

The melt viscosity of the toner obtained at 120°C was 1.5 x 10^4 poise, the charging amount was -19μc/g, and the number average particle size was 10.6μm.

The result of the image test showed that the toner attached to the heat roll in all the cases of the heat roll temperature of 180°C, 190°C, 200°C, 210°C, and 220°C and clear images were not obtained in each case.

Example 5

Production of Acrylic Resin

By following the same procedure as in Example 3 using 155 g of styrene, 220 g of methyl methacrylate, 100 g of 2-ethylhexyl acrylate, 25 g of acrylic acid, 400 g of toluene, and 100 g of isopropyl alcohol, a carboxyl group-containing acrylic resin having a glass transition temperature of 62°C, an acid value of 27.5 KOHmg/g, and a melt viscosity at 120°C of 2.1 x 10^4 poise was obtained.

The melt viscosity of the toner at 140°C was 7 x 10^4 poise, the charging amount was -18μc/g, and the number average particle size was 10.5μm.

Image Test

When the same test as in Example 3 was performed, no attaching of the toner to the heat roll was observed and the density retention of the images formed measured using a mending tape was at least 85%.

Comparison Example 5

By following the same procedure as in Example 5 except that the use of 2 parts of 1,3,5-tricyanatobenzene and 0.1 part of dibutyltin oxide was omitted, a tone was obtained.

The melt viscosity of the toner at 120°C was 5 x 10^4 poise, the charging amount was -18μc/g, and the number average particle size was 10.0μm.

The result of the image test showed that the toner attached to the heat roll in all the cases of the heat roll temperatures of 180°C, 190°C, 200°C, 210°C, and 220°C and clear images were not obtained in each case.

Example 6

Production of Acrylic Resin

By following the same procedure as in Example 5 except that the amounts of the monomers used were changed to 160 g of styrene, 230 g of methyl methacrylate, 105 g of 2-ethylhexyl acrylate, and 5 g of methacrylic acid, a carboxyl group-containing acrylic resin having a glass transition temperature of 46°C, an acid value of 6.3 KOHmg/g, and a melt viscosity at 120°C of 1.0 x 10^4 poise was obtained.

Production and Property of Toner

By following the same procedure as in Example 5 except that the above acrylic resin was used and also 4 parts of 4,4′-dicyanatobiphenyl was used in place of 1,3,5-tricyanatobenzene, a toner was obtained.

The melt viscosity of the toner at 140°C was 4.5 x 10^4 poise, the charging amount was 16μc/g, and the number average particle size was 10.6μm.

Image Test

When the same test as in Example 3 was performed, no attaching of the toner to the heat roll was observed and the density retention of the images measured by a mending tape was at least 85%.

Comparison Example 6

By following the same procedure as in Example 6 except that the use of 4 parts of 4,4′-dicyanatobiphenyl and 0.1 part of dibutyltin oxide was omitted, a toner was obtained.

The melt viscosity of the toner at 120°C was 2 x 10^4 poise, the charging amount was -18μc/g, and the number average particle size was 10.4μm.

The result of the image test showed that the toner attached to the heat roll in all the cases of the heat roll temperatures of 180°C, 190°C, 200°C, 210°C, and 220°C to cause offset and clear images were not obtained in each case.

Example 7

Production of Toner

By following the same procedure as in Example 1 except that 38 parts of an epoxy resin (Epikote 1004, trade name, made by Yuka Shell Epoxy Co.) of formula (1) described above having an epoxy equivalent of 900, n of about 2, and a melting point of 98°C and 50 parts of an epoxy resin (Epikote 1007, trade name, made by Yuka Shell Epoxy Co.) of formula (1) having an epoxy equivalent of 2,000, n of about 6, and a melting point of 128°C were used in place of the saturated polyester resin and further 2 parts of 1,3,5-tricyanatobenzene and 0.1 part of dibutyltin oxide were used in place of 2,2-bis(4-cyanatophenyl)propane, a toner was obtained.

Property of the Toner

The melt viscosity of the toner at 140°C was 2 x 10^4 poise, the charging amount was -18μc/g, and the number average particle size was 9.5μm.

Image Test

When the same test as in Example 1 was performed, no attaching of the toner to the heat roll was observed and the density retention of the images measured using a mending tape was at least 85%.

Comparison Example 7

By following the same procedure as in Example 7 except that the use of 2 parts of 1,3,5-tricyanatobenzene and 0.1 part of dibutyltin oxide was omitted, a toner was obtained.

The melt viscosity of the toner at 120°C was 3 x 10^4 poise, the charging amount was -22µc/g, and the number average particle size was 9.3µm.

The result of the image test showed that the toner attached to the heat roll in all the cases of the heat roll temperatures of 160°C, 170°C, 180°C 190°C, and 200°C to cause offset and clear images were not obtained in each case.

Example 8

Production of Toner

By following the same procedure as in Example 7 except that 44 parts of an epoxy resin (Epikote 1004, trade name, made by Yuka Shell Epoxy Co.) of formula (1) having an epoxy equivalent of 900, n of about 2, and a melting point of 98°C and 44 parts of an epoxy resin (Epikote 1009, trade name, made by Yuka Shell Epoxy Co.) of formula (1) having an epoxy equivalent of 2900, n of about 9, and a melting point of 148°C were used in place of the epoxy resins used in Example 7, respectively and further 2 parts of 1,3,6-tricyanatonaphthalene and 0.1 part of di-n-butyltin in place of 1,3,5-tricyanatobenzene and dibutyltin oxide, a toner was obtained.

Property of the Toner

The melt viscosity of the toner at 140°C was 2 x 10^4 poise, the charging amount was -25µc/g, and the number average particle size was 9.8µm.

Image Test

When the same test as in Example 7 was performed, no attaching of the toner to the heat roll was observed and the density retention of the images measured using a mending tape was at least 85%.

Comparison Example 8

The same procedure as in Example 8 was followed except that the use of 2 parts of 1,3,6-tricyanatonaphthalene and 0.1 part of di-n-butyltin was omitted, and a toner was obtained.

The melt viscosity of the toner at 100°C was 5 x 10^4 poise, the charging amount was -28µc/g, and the number average particle size was 9.3µm.

The result of the image test showed that the toner attached to the heat roll in all the cases of the heat roll temperatures of 160°C, 170°C, 180°C, 190°C, and 200°C to cause offset and clear images were not obtained in each case.

Example 9

0.5 Mol of terephthalic acid, 0.5 mol of isophthalic acid, 0.9 mol of ethylene glycol, 0.2 mol of diethylene glycol and 0.0003 mol of dibutyltin oxide were reacted at 160 - 220° C for 4 hours in a nitrogen gas atmosphere. Supply of nitrogen gas was stopped and reaction was further continued under a reduced pressure of 500 mmHg until the acid value became 5 KOHmg/g, thereby obtaining a polyester resin having a melt viscosity of 6 x 10^3 poise and a glass transition temperature of 59° C.

A toner was prepared according to Example 1, except that a mixture of the polyester resin obtained above and the polyester resin obtained in Example 1 was used in a weight ratio of 6 : 4.

The toner thus obtained was satisfied with both an offset resistance and a fixing property, and the result of an image test was good as same as in Example 1.

Example 10

By copolymerizing 250 g of styrene, 100 g of n-butyl acrylate, and 150 g of methyl methacrylate, an acrylic resin having no functional group (acid value 0) and a glass transition temperature of 55°C was obtained.

By following the same procedure as in Example 5 except that the acrylic resin thus obtained and the carboxyl group-containing acrylic resin as used in Example 5 were used at 1 : 1 in weight ratio, a toner was produced.

The charging amount of the toner was -17µc/g and the number average particle size was 10.4µm. The result of the image test using the toner was good as that of Example 5.

Example 11

By copolymerizing 410 g of methyl methacrylate and 90 g of n-butylacrylate using 150 g of methyl methacrylate, an acrylic resin having no functional group (glycidyl equivalent 0) and having a glass transition temperature of 61.3°C was obtained.

By following the same procedure as in Example 5 except that the acrylic resin thus obtained and the glycidyl group-containing acrylic resin as used in Example 3 were used at a 1 : 1 in weight ratio, a toner was produced.

The charging amount of the toner was -15µc/g and the number average particle size was 10.5µm.

The result of the image test was same as that in Example 5.

As described above in detail, in the toner of this invention, partial crosslinking network formation of a polyester resin, an acrylic resin, or an epoxy resin as the binder resin for the toner can be attained by a simple mixing operation at the preparation of the toner without use of polyfunctional monomers and hence an uncontrollable polymerization operation (i.e., partial crosslinking at polymerization) becomes unnecessary. Accordingly, an inexpensive polyester resin, acrylic resin, or epoxy resin can be used as the binder for the toner.

Also, the toner of this invention obtained using such a binder resin has a low-temperature fixing property and causes no offset phenomenon, which increases the practical value of the toner.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A toner for developing electrostatic images containing a resin selected from a saturated polyester resin, an acrylic resin, and an epoxy resin as a binder resin component, wherein said resin has a carboxyl group or a glycidyl group and is used as a resin composition containing (a) from 0.5 to 10 parts by weight of a polyfunctional cyanic acid ester having at least two cyanato groups in the molecule or a prepolymer of the cyanic acid ester per 100 parts by weight of the resin and (b) a curing catalyst for the component (a).

2. The toner of claim 1, wherein the curing catalyst (b) for the component (a) is previously compounded

in the resin composition in a step between the completion of the polymerization of the resin to the recovery (separation) of the polymerization product.

3. The toner of claim 1, wherein the curing catalyst (b) for the component (a) is an organic metal compound.

4. The toner of claim 1, wherein the resin composition is prepared by mixing components for the resin composition at a temperature of from 100°C to 200°C.

5. The toner of claim 1, wherein the resin composition is prepared by mixing a coloring agent with other necessary components for the toner.

6. The toner of claim 1, wherein the resin is a saturated polyester resin having a glass transition temperature of from 30°C to 75°C and an acid value of at least 10 KOHmg/g.

7. The toner of claim 1, wherein the resin is an acrylic resin having a glass transition temperature of from 30°C to 75°C and an acid value of from 2 to 50 KOHmg/g.

8. The toner of claim 1, wherein the resin is an acrylic resin having a glass transition temperature of from 30°C to 75°C and a glycidyl group equivalent of from 1,000 to 20,000.

9. The toner of claim 1, wherein the resin is a bisphenol A type epoxy resin having a melting point of from 60°C to 160°C.